APPLICABILITY OF THE AVAILABLE SORPTION MODELS FOR PREDICTING MERCURY REMOVAL

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By

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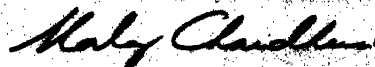
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CERTIFICATE

Certified that the work presented in this thesis entitled "Applicability of the Available Sorption Models for Predicting Mercury Removal" by Sri Sanjoy Kumar Bhattacharya has been carried out under my supervision and has not been submitted elsewhere for a degree.

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MODELS FOR PREDICTING MERCURY REMOVAL

ABSTRACT

All the investigations reported todate in the area of heavy metal removal from water were concerned mainly with gross removal efficiencies and no attempts were made to formulate any generalized mathematical approach for predicting the performance of sorption systems. On the contrary, the organics-sorption understanding has progressed considerably during the last decade and many mathematical models have been proposed by different workers to predict performance characteristics of sorption systems. In the present study, a comprehensive listing of the available sorption models was prepared and on the basis of the available data two modified approaches were proposed to predict the effluent concentration-time profiles for mercury-coal and mercury-active carbon systems. The Thomas solution for the second-order kinetics supplemented by Hiester and Vermeulen, using theoretical as well as graphical methods for the evaluation of the sorption rate constant, constituted the first approach. In the second approach the original lumped parameter method used by Keinath was modified into a nondimensional form and the equations were solved numerically by the fourth order Runga-Kutta method. Weighing the modified approaches with the limited data available revealed that the first approach could reasonably predict the performance of mercury sorption systems with influent concentration in the milligram range. The second approach, i.e., the modified lumped parameter approach predicted a pretty early breakthrough. The limitations of the two proposed approaches were discussed in light of the difficulties involved in reliable estimation of the different model parameters.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

After the Minamata mercury pollution episode in Japan in 1953, heavy metal pollution began to concern the guardians of public health. Their possible presence in the ecosystem and the environmental effects of mercury, lead, cadmium, chromium, silver, etc. were investigated. The analytical methods including instrumental analysis for detecting minute concentrations of these metals were studied and improved upon. Analysis of low concentrations of heavy metal compounds is very difficult but significant even for fixing up their permissible limits in drinking water. Atomic absorption spectrophotometry is recognized presently as the most reliable of all the proposed methods (Standard Methods, 1975). Once the analysis part was performed confidently the environmental engineers started investigating the efficacies of the conventional water and wastewater treatment processes in removing heavy metals (Logsdon and Symons, 1973).

The first major challenge to the environmental engineers was thrown by the epidemic diseases which was pretty well tackled by including the chlorination step with the traditional treatment processes (McCarty, 1980). The second challenge was thrown by the organics. This time too they emerged winners by virtue of the grand success of active carbon sorption of organics. If heavy metal pollution is considered to be the next big challenge, it should be admitted that the

fight is still continuing as workers in this field are busy studying the removal efficiencies and mechanisms of removal by the different processes.

It has been observed that active carbon which played the trick for organics removal, does also adsorb heavy metals but the extent of removal is definitely lesser. In the case of mercury removal, this led some workers to opt for cheaper sorbents like wool, hair, rubber, coal etc. (Michelsen and co-workers, 1975; Pandey and Chaudhuri, 1981). But all these studies on heavy metal removal by sorption are rather qualitative and limited to specific systems only. On the other hand, the sophistication of organics-sorption research has increased by leaps and bounds during the last decade and a number of complex mathematical approaches have been proposed (Crittenden and Weber, 1978a; Keinath and Weber, 1968; Keinath, 1975; McKay, Otterburn and Sweeney, 1980; Wilson and Clarke, 1979), most of them being solved numerically with modern computers.

To keep pace with the progress in organics-sorption research it was felt that the available sorption models should be compiled and their potential applicability for predicting heavy metal removal should be investigated. It would be logical, as a first step, to include the pure, single-solute models to be followed by the more complex models developed for bi- and multi-solute systems. Such an approach should ultimately lead to a more appropriate model taking into consideration the limitations of the existing models developed for

organics sorption. The present study was limited to the first step with particular reference to mercury. The models are listed here and the ones developed for pure, single-solute systems are assessed for application to the mercury sorption system ultimately leading to some modified approaches for final weighing using the data reported by Humenick and Schnoor (1974) and Pandey (1978) for mercury-active carbon and mercury-coal systems, respectively.

2. AVAILABLE SORPTION MODELS

During the last decade numerous models have been proposed to explain sorption of organics and dyes onto active carbon. These models range from mathematical and conceptual descriptions of breakthrough curve and numeric solution models (Crittenden and Weber, 1978a) to detailed investigations of the thermodynamic properties of the solvents, sorbents and sorbates (McGuire and Suffet, 1978). The models are not equivalent in data needs, theoretical justifications or applications, but are useful as a basis for understanding the sorption mechanism. A complete list of the available models is presented here. It is interesting to note, however, that till now none of these models has been applied to heavy metal sorption. The discussion following the list also includes preliminary assessment of the models to qualify their selection for a more detailed weighing using the available data on mercury sorption.

Model	Reference
A. Old Models	Swan and Urquhart (1927)
a. Lagergren Rate Equation (1898)	
b. Arrhenius Equation (1910)	
c. Pickles Equation (1920)	
d. Gustaver Equation (1922)	

Model	Reference
B. Conceptual Models	McGuire and Suffet (1973)
a. Mass Transf : Zone	
b. Ideal Adsorbed Solution (IAS) Theory	
c. Net Adsorption Energy Concept	
C. Michigan Adsorption Design and Applications Model (MADAM)	Crittenden and Weber (1978a)
D. Logistic Curve	Oulman (1980)
E. Diffusion Model	McKay, Otterburn and Sweeney (1980)
F. Keinath Model	Keinath (1975)
G. Wilson and Clarke Model	Wilson and Clarke (1979)
H. Second Order Kinetics Using Thomas Solution	Thomas (1944)
I. Miyamoto and Tram Model	Miyamoto and Tram (1979)
J. Famularo Concept	Famularo, Mueller and Pannu (1980)
K. Convection Limited Model	Hendricks (1980)

A. Old Models

Swan and Urquhart (1927) gave a very comprehensive review of the contemporary sorption models available in the first quarter of the present century. Out of a very long list given, the following four models were subjected to a preliminary assessment using the available data on mercury removal reported by Humenick and Schnoor (1974; and Pandey (1978).

    a. Lagergren Rate Equation

$$\frac{dx}{dt} = k(x_{eqm} - x_t) \tag{1}$$

where, k = rate of sorption,

x_{eqm} = mass of sorbate sorbed by unit weight of sorbent at equilibrium, and

x_t = mass of sorbate sorbed by unit weight of sorbent at time, t.

This equation does not conform to general requirements of the rate equation and Gustaver (Swan and Urquhart, 1927) had pointed out that it is inapplicable to high concentrations, since it assumes constancy of concentrations during sorption.

b. Arrhenius Equation

$$\log \frac{s}{s - x} - 0.4343 \frac{x}{s} = kC \tag{2}$$

where, C = equilibrium concentration of solution,

s = mass of sorbate sorbed per unit weight of sorbent at saturation, and

x = mass of sorbate sorbed per unit weight of sorbent.

c. Pickles Equation

$$k = \frac{1}{t_2 - t_1} - \log \frac{a - x_1}{a - x_2} - 0.4343 \frac{x_2 - x_1}{a} \tag{3}$$

where, a = original amount of sorbate, and

x_1, x_2 = mass of sorbate sorbed per unit weight of sorbent at time t_1, t_2.

This equation had been used for sorption from gas as well as from liquid.

d. Gustaver Equation

$$k = \frac{1}{t(a - x_{eqm})} \log\left(\frac{a - x}{x_{eqm} - x} \cdot \frac{x_{eqm}}{a}\right) \tag{4}$$

Gustaver obtained the equation by assuming that the amount of
sorption was proportional to the free surface and the total
amount of sorbate in the liquid phase.

All the above four models are empirical and applicable
to specific systems only. They were found unsuitable for
application to the mercury system on the basis of preliminary
assessment. The detailed analysis, however, is not presented
here.

B. Conceptual Models

    a. Mass Transfer Zone

        The height and rate of movement of the mass transfer
zone in an active carbon column was used to characterize the
effects of the process variables on sorption of organics
(McGuire and Suffet, 1978). The height of the mass transfer
zone is a measure of the rate of removal of the solute by
the sorbent and the rate of movement of the mass transfer
zone is a measure of the affinity of the solute for the sorbent
surface. The model is applicable when the solute has a rela-
tively high affinity for the sorbent surface. Attempts to
use the mass transfer zone concept to define the breakthrough
characteristics of poorly sorbed organics were unsuccessful.
As heavy metals do not have a very high affinity for active
carbon this model was not considered any further in this
study.

    b. Ideal Adsorbed Solution (IAS) Theory

        This theory describes a correlation for estimating
the sorption of organic compounds from dilute aqueous solutions

onto active carbon (McGuire and Suffet, 1978). A formal statistical-mechanical treatment of sorption from dilute solutions provided the basic equation to develop the correlation. Developing the correlation for mercury-sorbent systems was considered to be beyond the scope of the present study.

    c. Net Adsorption Energy Concept

    The calculated net adsorption energy is a function of a compound's aqueous solubility, molecular weight, density, dispersion component of the solubility parameter for the organic compound and that for the active carbon surface. This concept was used to evaluate sorption data for medium-polarity to high-polarity organic compounds and to relate that to other sorption data in the literature so that a general understanding of sorption could be approached through an understanding of compounds and surface polarities (McGuire and Suffet, 1978). For the mercury-active carbon or mercury-coal systems this understanding about the compound and surface polarities are not very clear and hence the net adsorption energy concept cannot be applied at present.

C. Michigan Adsorption Design and Applications Model (MADAM)

    Crittenden and Weber (1978a) developed the Michigan Design and Applications Model (MADAM) to facilitate performance forecasting for optimum design of sorption systems and for use as a predictive component of a feed-forward operational control system. They described conceptual and mathematical bases underlying the model, techniques used for parameter estimation and methodologies for determination of surface

diffusion coefficients and film transfer coefficients. They
also tested the models for single- and multi-component
solutions using independently determined model parameters
(Crittenden and Weber, 1978b). It was projected that complex
factors such as fluid dispersion, solids-mixing, multi-solute
interactions and surface biological growths, could eventually
be incorporated into the numeric solutions. The partial
differential equation for liquid-phase material balance was
simplified and the numeric method, the implicit finite back-
ward difference method was compared by Weber and Crittenden
(1975) to the famous analytical solution proposed by Thomas
(1944). They found that the solutions gave almost identical
traces when plotted and that the error was much less than
one percent. For solution of solid-phase partial differential
equation, the Crank-Nicholson method was selected. The influent
and effluent concentration-time profiles were given for phenol,
p-bromophenol, p-toluene sulfonate and dodecyl benzene
sulfonate (Crittenden and Weber, 1978b).

The solutions provided in the publications referred to
above, are not non-dimensional. So these solutions could
not be applied for mercury-active carbon or mercury-coal
system. The computer programs for the solution have not been
published. So if one wants to apply the MADAM for mercury
sorption then one would have to solve the liquid- and solid-
phase partial differential equations by the implicit finite
backward difference and Crank-Nicholson methods respectively,
which was considered to be beyond the scope of the present work.

D. Logistic Curve

The logistic curve was proposed as a model for determining the design parameters for active carbon columns (Oulman, 1980). The parameters were used for scaling up the design of a carbon column from laboratory and pilot scale to full scale.

The Bohart-Adams equation was published in 1920 for predicting the service life of the active carbon used in a gas mask for the removal of chlorine from air. The equation can be written as

$$\ln(\frac{C_o}{C} - 1) = K'Nx_d/v - K'C_ot \tag{5}$$

where, C = effluent concentration,

C_o = influent concentration,

K' = sorption rate coefficient,

N = sorption capacity coefficient,

x_d = bed depth,

v = approach velocity (rate of application), and

t = service time.

Equation (5) can be rewritten as

$$\frac{C}{C_o} = \frac{1}{1 + e^{-(a + bt)}} \tag{6}$$

The plot of C/C_o vs. t is the Logistic Curve which is S-shaped.

The data from a sorption run can also be linearized according to equation (5) by plotting $\ln(C/C_o - 1)$ vs. t. Although this is a perfectly satisfactory way of handling the data, biologists have been using the inverse expression for many years in linearizing dose response relationship

$$\ln(\frac{C/C_o}{1 - C/C_o}) = -K'Nx_d/v + K'C_o t \tag{7}$$

The left hand side of equation (7) is called the "logit" of C/C_o which is the contraction of the term "logistical unit". From the plot of logit of C/C_o against t, average values of K and N can be calculated which may be used in predicting full scale plant performance.

The column studies on mercury sorption reported by Humenick and Schnoor (1974) and Pandey (1978) were not continued upto breakthrough. So logit of C/C_o remained almost a constant and it was not possible to calculate K and N, the sorption rate and capacity coefficients.

E. Diffusion Model

A school of thought (McKay, Otterburn and Sweeney, 1980) believes that the mechanism of sorption involves a study of the diffusional processes. Fick's second law of diffusion in terms of spherical polar co-ordinates r, θ and ϕ is given by (Crank, 1956)

$$\frac{dC}{dt} = \frac{1}{r^2}[\frac{\partial}{\partial r} Dr^2 \frac{\partial C}{\partial r} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} D \sin\theta \frac{\partial C}{\partial\theta} + \frac{D}{\sin^2\theta} \frac{\partial^2 C}{\partial\phi^2}] \tag{8}$$

where, D = molecular diffusivity.

The following assumptions were made for solving the equation (Skelland, 1974): (i) The concentration of solute is uniform at C_o throughout the solution and is zero in the sorbent particle at the start of diffusion (t = 0), (ii) The resistance to transfer in the medium surrounding is negligible, and

(iii) Diffusion is radial, there being no variation in concentration with angular position. The equation was solved using the initial assumption which specify the boundary conditions as $C_{a,o} = C_o$ and $C_{r,\infty} = C_\infty$ where, r = particle radius, and C_∞ = equilibrium concentration. The fraction solute sorption onto the sphere at time t is given in equation (9) where $\bar{C}$ is the average solute concentration throughout the sphere at time t

$$\frac{C_o - \bar{C}}{C_o - C_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - (\frac{Dn^2 \pi^2 t}{r^2}) \tag{9}$$

where, n = an integer.

A numerical solution is found in the literature (Newman, 1931) in the form of a plot of $1 - (C_o - \bar{C})/(C_o - C_\infty)$ vs. Dt/r^2 (Fig. 1). The solution is non-dimensional and is, therefore, apparently very useful for application to the mercury systems under consideration. But the crux of the problem, which causes the limitation to this model, lies in the difficulty in determining the actual value of the diffusivity. When intraparticle diffusion is accompanied by sorption, as in the case of the mercury systems, evaluation of characteristic diffusivities from experimental rate data can be accomplished only by appropriate modification of Fick's law for diffusion to include a term for the sorption process (Weber, 1972). If the relationship between the concentration of sorbed solute and solute free to diffuse is linear, the modification of Fick's law still permits rather steady analytic solution for the characteristic diffusivity. If the
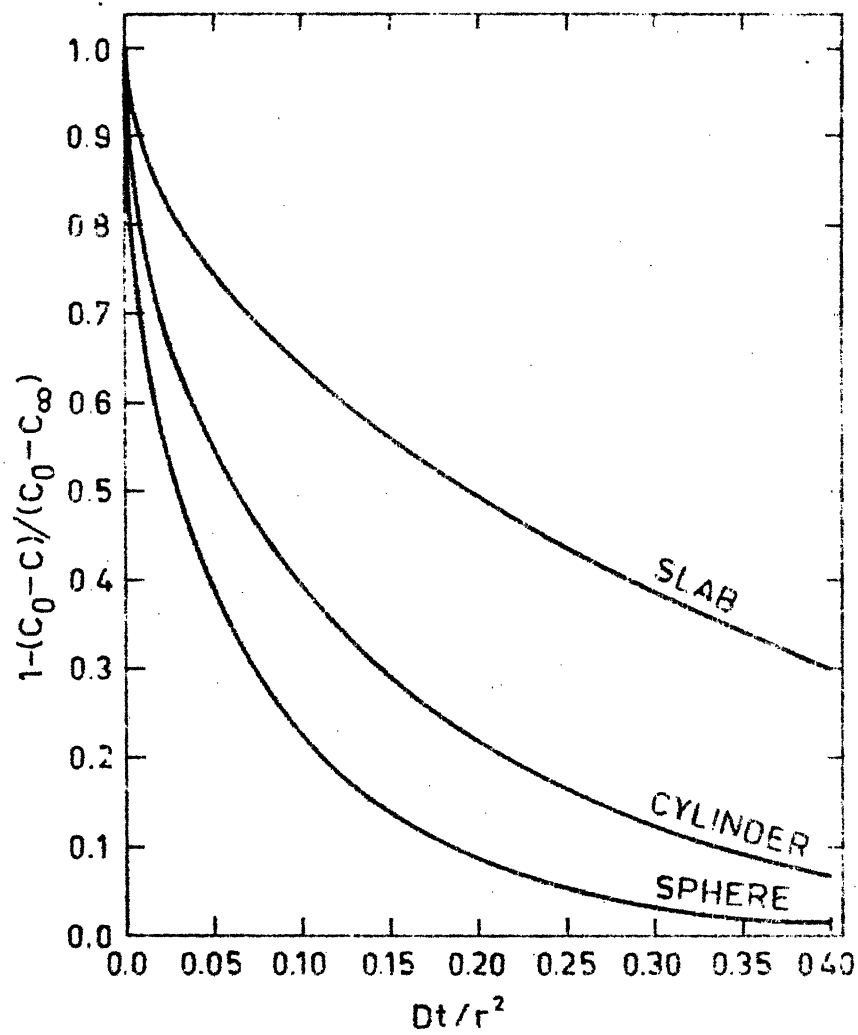
FIG. 1   UNSTEADY-STATE MOLECULAR DIFFUSION
IN A SPHERE, SLAB OR CYLINDER
(Newman, 1931).

relationship between free and sorbed solute is nonlinear, as in the mercury systems, the resulting modification of the expression for Fick's law is nonlinear and numerical integration methods must be used to obtain a solution for the characteristic diffusion coefficient (Weber, 1972).

F. Keinath Model

Keinath (1975) published a quite detailed discussion of the modeling of sorption contactors by means of a lumped parameter approach and included computer programs for carrying out these calculations.

From material balance relationship for a packed-bed case, the developed partial differential equation upon simplification becomes

$$U \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = 0 \tag{10}$$

where, U = solution volumetric flow rate, l/hr,

C = solution-phase concentration of solute, mole/l,

q = solid-phase concentration of solute, mole/g,

z = axial distance, cm,

ε = void ratio, and,

t = time, hr.

Keinath (1975), instead of solving this equation, adapted the lumped parameter approach through the use of a continuous system modeling program, CSMP/360, produced by IBM. Solutions are given for four cases, viz., i) single-solute system, constant input, ii) single-solute system, sine-curve flow input, iii) single-solute, countercurrent system, and

iv) di-solute system. As the available data for mercury-sorbent systems are for the single-solute system with constant input, only the first case is discussed here.

Use of the lumped parameter approach required segmentation of the packed-bed of sorbent into a discrete number of finite elements (Friedly, 1972). Keinath divided his column length (about 32.4 cm) into ten such elements. Both the liquid- and solid-phase concentrations of solute were assumed to be uniform throughout each element. Maintaining continuity of mass flow of the solute between adjoining elements was also important for both the liquid and solid phases. Keinath (1975) proposed the following formulation for an element of the packed-bed

	Solution-phase	Solid-phase
Input to element	UC_{n-1}	0
Output from element	UC_n	0
Sorption	$\rho R_A V$	$\rho R_A V$
Accumulation	$\varepsilon (dC_n/dt)V$	$\rho (dq_n/dt)V$

where, V = volume of elements, liters,

R_A = rate of sorption, mole/g-hr, and

n = number of elements.

From material balance:

Input to element = Output from element + Sorption
+ Accumulation

The final equations

$$\frac{dC_n}{dt} = \left(\frac{U}{\varepsilon V}\right)(C_{n-1} - C_n) - (\rho/\varepsilon)R_A \qquad (11)$$

$$\frac{dq_n}{dt} = R_A \tag{12}$$

Thus, adapting the lumped parameter approach facilitated elimination of the partial differential equation. The essence of Keinath approach was the development of equations (11) and (12) and solving them in a straightforward manner by using CSMP/360.

If the CSMP/360 program were available, application of Keinath model for the mercury systems would have been easier. Since this program was not available in the dec-10 system at IIT-Kanpur, direct application of Keinath approach was not possible. In spite of this setback, attempts were made to solve the equations by the fourth order Runga-Kutta method (Chapter 4), very standard numerical method for solving ordinary differential equations. With a view to making a general approach, the equations were modified into their non-dimensional form (Chapter 4).

G. Wilson and Clarke Model

This model was also based on the lumped parameter approach like the Keinath model. Sorption of solutes onto active carbon was modeled at the microscopic levels by means of the equations of continuity and mass balance. Two competing solutes were assumed to be present. The results of this approach were then compared with the much simpler lumped parameter model for active carbon sorption for two competing solutes. Quite good agreement was obtained validating the utility of the simpler model (Wilson and Clarke, 1979; Wilson, 1979).

The available data for the mercury systems being for pure, single-solute systems only, the Wilson and Clarke model framed for bi-solute systems was not included in the present work. As an example of the lumped parameter approach, only the Keinath model was studied in details.

H. Second-order Kinetics Using Thomas Solution

The rate equation (13) and the conservation of mass equation (14) together provide a description of the mass-transfer process sufficient to permit a mathematical solution (Weber, 1972)

$$\frac{d(q/q_\infty)}{dT} = \frac{C}{C_o}(1 - \frac{q}{q_\infty}) - r\frac{q}{q_\infty}(1 - \frac{C}{C_o}) \tag{13}$$

$$\frac{t}{s} = \frac{C_o(V - vf_E)}{q_\infty \, \rho_b \, v} \tag{14}$$

where, r = equilibrium parameter = $\dfrac{1}{1 + KC_o}$,

s = column capacity parameter = $\dfrac{k\,\rho_b\,KSL}{v_1}$,

t = solution capacity parameter =

$$\frac{kf_E}{\rho_b S}(\frac{1}{K} + C_o)(\frac{V - vf_E}{R}) ,$$

v = bulk volume of column, under consideration,

v_1 = macroscopic water flow velocity,

V = total volume of feed that has entered the column ,

ρ_b = density of dry sorbent in column,

f_E = fraction of external voids per unit volume of the sorbent packed,

$$k = \text{sorption rate constant,}$$

$$K = \text{Langmuir isotherm constant,}$$

$$L = \text{length of column,}$$

$$R = \text{volumetric flow rate of fluid through fixed sorbent, and}$$

$$S = \text{ultimate capacity of dry sorbent.}$$

These equations were integrated, subject to appropriate boundary conditions, by a method described by Thomas (1944) to yield the following expression for the ratio of the concentrations of solute in the effluent stream, C, to the initial concentration in the influent stream, C_o, for any specified combination of the parameters r, s and t

$$\frac{C}{C_o} = \frac{J(rs,t)}{J(rs,t) + [1 - J(s,rt)] \exp[(r-1)(t-s)]} \tag{15}$$

where, $J(x,y) = 1 - e^{-y} \int_0^x e^{-z} I_o(2\sqrt{yz})dz,$

x, y and z = integral variables, and

I_o = modified Bessel function of the first kind.

Among the usable mathematical approaches for prediction of effluent concentration in a column system, the method of Thomas (1944) has the greatest generality, because only this method takes into account the full range of possible variations in equilibrium constants for sorption reactions (Hiester and Vermeulen, 1952; Vermeulen, 1958; Vermeulen, Klein and Hiester, 1973; Vilker and co-workers, 1978). The theory of Thomas has escaped the use it deserves mainly because of the functions

which are apparently difficult to evaluate. Hiester and Vermeulen (1952) gave the following workable form of the expression originally developed by Thomas (1944)

$$\frac{C_o}{C} - 1 =$$

$$\frac{\sqrt{\pi} \; [1 - H(\sqrt{rt} - \sqrt{s})] \; \exp(\sqrt{rt} - \sqrt{s})^2 - [1/(\sqrt{rt} + \sqrt[4]{rst})]}{\sqrt{\pi} \; [1 - H(\sqrt{rs} - \sqrt{t})] \; \exp(\sqrt{rs} - \sqrt{t})^2 + [1/(\sqrt{t} + \sqrt[4]{rst})]}$$

(16)

where, $H(z)$ = error function.

The error functions may be noted from the tabulated value and the value of the whole expression may be calculated using a pocket calculator. Hiester and Vermeulen (1952) also published plots of C/C_o against t/s for r = 0.0, 0.5, 1.0, 2.0, 10.0 and 100.0 (Graph for r = 1 is shown in Fig. 2).

In fine, the procedure for predicting the concentration profile for a column system is as follows

i)   r, s and t are calculated from their known expressions,

ii) if r has any of the values for which graphs are available, the appropriate graph is taken and the C/C_o values are predicted for the known values of s and t/s (Fig. 2), and

iii) if r has some other value, the expression (16) is directly evaluated by using the tabulated values of error functions.

Looking carefully into the above procedure it is obvious that as far as calculations are concerned, the crux of the problem lies in finding true values of the parameters s and t. If one looks back into the expressions for s and t
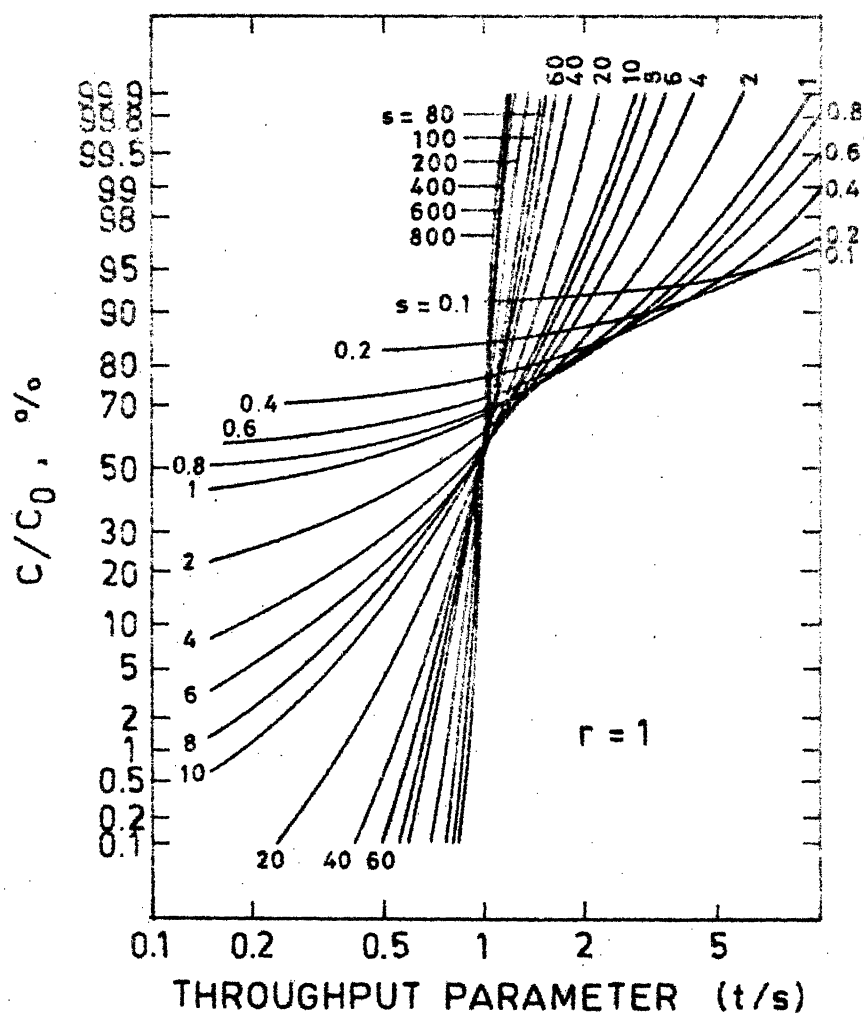
FIG. 2 GENERALISED BREAKTROUGH CURVES
(Hiester and Vermeulen, 1952).

$$s = \frac{k \rho_b \, KSL}{v_1} \qquad (17)$$

$$t = \frac{kf_E}{\rho_b S} \left(\frac{1}{K} + C_o\right)\left(\frac{V - vf_E}{R}\right) \qquad (18)$$

one finds that all the terms except k are either known or may be found out experimentally. The available expression for k is as follows (Hiester and Vermeulen, 1952)

$$\frac{1}{K} = \frac{1 + (r-1)(q/q_\infty)}{k_F a_F} + \frac{(1-r)(C/C_o) + r}{k_P a_P D_G} \qquad (19)$$

where, k_F = mass transfer coefficient for case of fluid-
phase transfer controlling,

k_P = mass transfer coefficient for case of transfer
inside solid particles,

a_F, a_P = effective areas for mass transfer for the
respective cases, and

$$D_G = \frac{q_\infty \, b}{C_o \, f_E} = \text{ratio of concentrations on solid-}$$
and in liquid-phases at saturation.

So now for finding the true values of the parameters s and t, one would have to determine the transfer coefficients and the effective areas. The determination of the transfer coeff-icients, even though very difficult, is facilitated by the available expressions (Keinath, 1975)

$$k_P a_P = \frac{60 \, D_{pore}}{D_P^2} (1 - f_E) \qquad (20)$$

where, D_p = particle diameter,

$$f_E \quad = \text{porosity, and}$$

$$D_{pore} = \text{pore diffusivity term.}$$

Again, determination of the value of the pore diffusivity term
is difficult

$$D_{pore} \quad = \quad \frac{D_1 \, f_I}{2} \tag{21}$$

where, D_1 = diffusivity of solute in solvent, and

f_I = internal porosity.

The other mass transfer coefficient k_F may be determined from
expressions containing Reynolds number, Sherwood number and Schmidt
number. This method of finding k_F was used by Keinath (1975).
The other method (Famularo, Mueller and Pannu, 1980) of
finding k_F is based on the following equation

$$\ln \frac{C}{C_o} \quad = \quad - \frac{k_F \, a_F}{V} \, t \tag{22}$$

where, V = batch volume of liquid.

At the beginning of a batch rate run when the solid-phase
concentration is very small, it can be shown that liquid
resistance clearly controls the overall transport of solute
into the particle (Famularo, Mueller and Pannu, 1980). Under
this condition only the equation (22) is applicable for deter-
mining k_F.

Coming back to the problem of evaluating the parameters
s and t, one may comment, perhaps without being pragmatic,
that these very sensitive parameters can never be determined
without reservations and hence the potential of Thomas solution
is reduced significantly by this weakest link.

I. Miyamoto and Tram Model

To eliminate the just discussed indirect method of determining the sorption rate constant, k, Miyamoto and Tram (1979) proposed a direct graphical method. They studied the sorption of a dispersed dye by sand and calcareous soil using laboratory batch and column tests for the purpose of obtaining quantitative information needed for disposing of dyeing effluent. Miyamoto and Tram (1979) proposed the following rate equation for sorption data fitting well with the Langmuir isotherm

$$\frac{\partial s}{\partial t} = k\left[K(S - s)C - s\right] \tag{23}$$

where, k = sorption rate constant,

S = ultimate capacity of dry adsorbent,

K = Langmuir isotherm constant,

s = amount of sorbate sorbed, and

C = equilibrium dye concentration.

At equilibrium, $\frac{\partial s}{\partial t} = 0$. Thus, the right hand side of equation (23) reduces to

$$s = K(S - s)C \tag{24}$$

The equation (24) is nothing but the representation of Langmuir sorption isotherm. From the law of mass conservation

$$\frac{\partial c}{\partial t} = -\varepsilon \frac{\partial s}{\partial t} \tag{25}$$

$$\varepsilon s(t) = C_o - C(t) \tag{26}$$

where, ε = soil/solution ratio.

Using equations (25) and (26), the equation (23) was rewritten as

$$\frac{\partial c}{\partial t} = - k\left[KC^2 + (\varepsilon\, KS - KC_o + 1)C - C_o\right] \tag{27}$$

Integrating equation (27) from t = 0 to t = t and from C = C_o to C = C

$$\ln(2KC_o + \alpha + \beta)(2KC + \alpha - \beta)/(2KC_o + \alpha - \beta)(2KC + \alpha + \beta)$$

$$= -\beta\, kt \tag{28}$$

or $\ln X = -\beta\, kt$

where, $\alpha = \varepsilon\, KS - KC_o + 1$, and
$$\beta = (4KC_o + \alpha^2)^{1/2}.$$

If the plot of $(-1/\beta)\ln X$ against t is linear (Fig. 4a) then the rate constant k can be determined from the slope of the plot. The rate constant was determined for mercury-coal system and was used in Thomas solution to determine the column and solution capacity parameters s and t (Chapter 4).

J. Famularo Concept

Famularo, Mueller and Pannu (1980) conceptually described the carbon models, viz., homogeneous solid diffusion model, pore diffusion model and uniform state model. They proposed a micropore-macroshell particle concept. The decline in concentration, according to them could roughly be divided into an initial high-rate interval followed by a lower rate approach to equilibrium. Such behavior is consistent with the porous nature of active carbon and can be attributed to a high

rate of solute movement through macropores followed by much slower passage through micropores. The detailed model (Famularo, Mueller and Pannu, 1980) was not considered in this study as it involves several mass transfer coefficients and other parameters which are difficult to determine for mercury-sorbent systems.

K. Convection Limited Model

The ancillary kinetic models focus upon the various diffusion mechanisms at the particle level, e.g., film diffusion, pore diffusion and pore-surface diffusion. Another sorption rate mechanism not considered thus far is the bulk transport of sorbate to the particle by convection (Hendricks, 1980). The convection limited model supplements the established theory based upon the material balance equation and particle kinetics. The theory is applicable particularly to the design of packed-bed sorption reactors in which the sorbate feed concentrations are very low and this model should be applicable for removal of low concentrations of heavy metals from drinking water. For low concentrations of sorbate, if the sorption rate is calculated on the basis of diffusion only the predicted rate would be higher than the actual rate.

The available mercury-sorption data were not sufficient for testing this model and hence the potential of this very interesting model remained undetermined at this stage.

3. SPECIAL ASPECTS RELATED TO MERCURY SORPTION

This chapter includes a discussion on some special
aspects that need to be included or taken into consideration
while attempting to predict mercury removal through the use of
mathematical modeling. A section on the possible hazards of
active carbon or charcoal as sorbent in water treatment is
also included.

A. Species Distribution of Mercury Compounds in Water

When Hg^{++} and Cl^- are present in water they will combine
to form the undissociated but soluble species of $HgCl_2$.
Chloride can also combine with mercury in other proportions
to form a variety of complexes and equilibrium relationships
can be developed for the various mercury-chloride species
from the following reactions (Sawyer and McCarty, 1978)

$$Hg^{++} + Cl^- \rightleftharpoons HgCl^+ ; \quad K_1 = 5.6 \times 10^6$$

$$HgCl^+ + Cl^- \rightleftharpoons HgCl_2 ; \quad K_2 = 3.0 \times 10^6$$

$$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^- ; \quad K_3 = 7.1$$

$$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{--} ; \quad K_4 = 10.0$$
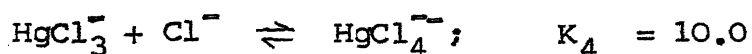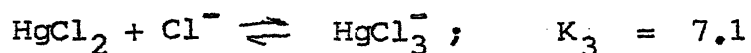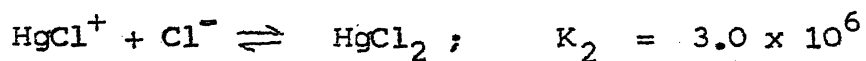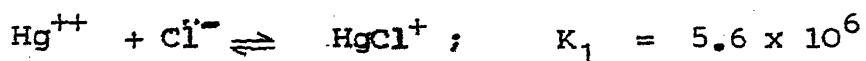
Reimers, Krenkel and Eagle (1974) gave a table showing the
species distribution of the inorganic forms of mercury under
different conditions of chloride concentrations and pH.

Chloride Concentration	Species of Inorganic Mercury		
	pH = 5	pH = 7	pH = 9
18000 ppm	$HgCl_4^{--}$	$HgCl_4^{--}$	$HgO.H_2O$
10000 ppm	$HgCl_4^{--}$	$HgCl_4^{--}$	$HgO.H_2O$
100 ppm	$HgCl_2$	$HgO.H_2O$	$HgO.H_2O$

According to Morris and Weber (1966), intraparticle transport phenomena may derive from the net action of several molecular forces. For most systems of interest in water and waste treatment applications, these forces may be enumerated as sorption, two and three dimensional micelle formation, electrokinetic interactions and molecular diffusion (Weber, 1972). In the studies of organics-sorption, the electrokinetic interaction was neglected in general. But in the case of mercury-sorption, from the preceding discussion on species distribution, it is apparent that electrokinetic interaction between mercury complexes and the active carbon or coal surface is significant. Active carbon and coal surfaces are generally considered to bear net negative charges (Bean, Campbell and Anspach, 1964; Pandey, 1978). Thus, for successful prediction of mercury concentration-time profiles in a column system, the applied model should be incorporated with the contribution of electrokinetic interaction. However, this would make the model more complex leading to difficulty in mathematical solution.

Referring to the Famularo concept of micropore-macroshell particle (Famularo, Mueller and Pannu, 1980) it is recognized that the sizes of the different mercury complexes are also important for sorption. The mercury complexes may fail to enter into the minute pores even if the potential for sorption and electrokinetic attractions are there. If the mercury species have restricted entry into the pores of the sorbent because of size consideration, the whole concept of sorption, electrokinetic interaction and diffusion is no more totally valid.

B. Forms of Mercury — Inorganic, Organic and Chelated Species

The potential for microbial methylation of mercury by fungi and bacteria exists under aerobic as well as anaerobic conditions (Jernelov, Landner and Larsson, 1975). In a column containing the sorbent, the inorganic mercury coming in as feed might be transformed into organic mercury. This possibility brings in two problems, viz., a) the model selected for only inorganic mercury removal becomes insensitive and a new bacteriologically activated carbon model similar to that of Ying and Weber (1979) needs to be applied, and b) even though organic mercury removal is more than that of inorganic mercury by the same system, the advantage is only apparent because the small amount of organic mercury present in the effluent might be more hazardous compared to the higher concentrations of inorganic mercury in the column-feed.

Prediction of the actual environment inside the column is rather difficult. Apparently, aerobic environment should

prevail in the column for a continuous feed system as the influent has sufficient dissolved oxygen. On the other hand, active carbon through some mechanism has the ability to preferentially adsorb oxygen from air and oxygen deficiencies might occur even in the complete absence of biological activity (Strudgeon and Lewis, 1980). If the dissolved oxygen content of the column influent and effluent are known, predictions about the inside environment may be made. However, the possibility of existence of some anaerobic regions cannot be ruled out even if the column effluent contains detectable levels of dissolved oxygen.

The reported removal of Hg(II) by either active carbon or coal system was not very high (Humenick and Schnoor, 1974; Pandey, 1978). Thiem, Badorek and O'Connor (1976) treated aqueous solutions of mercury with various combinations of active carbon, EDTA, tannic acid, citric acid and calcium. The results of their experiments indicated that the presence of chelating agents enhanced the removal of mercury from water using powdered active carbon as sorbent. Now if in column systems also chelating agents are added, the predicted concentration-time profile on the basis of carbon-only system would be different. Moreover, it would be extremely difficult to propose and/or apply a mathematical sorption model incorporating the contribution of the chelating agents.

C. Attainment of Equilibrium

Extended contacting periods should be allowed during isotherm evaluations to ensure that equilibrium is attained;

wherever possible, powdered active carbon isotherms should be used instead of granular carbon isotherms (Peel and Benedek, 1980). Isotherm data are very important for column-system effluent prediction. The available isotherm data for mercury (Humenick and Schnoor, 1974; Pandey, 1978) were not generated with the powdered form of the sorbent and it was not known whether true equilibrium had been attained because sometimes it may take even five weeks to attain true equilibrium (Peel and Benedek, 1980).

D. Analysis of Mercury

Methods for analysis of total mercury have been a matter of toxicological concern and the subject of numerous reviews for many decades (Reimers, Burrows and Krenkel, 1973). The methods have proliferated with the introduction of refined instrumentation, e.g., atomic absorption, neutron activation, X-ray fluorescence and mass spectroscopy, and electrokinetic techniques. Low concentrations of trace metals can now be determined with precision. The different methods of mercury analysis reported in the literature (Ballard and Thornton, 1941; Fishman, 1970; Chau and Saitoh, 1970; Elly, 1973; Standard Methods, 1975; Jackson and Dellar, 1979) are not discussed here. Greenberg, Thomas and Tamplin (1973) gave a table showing the comparison of some of the commonly used methods. The table, being considered to be an important reference for selection of methods, is presented here.

	Flameless Atomic Absorption	Crystal Violet	Mercury Analyzer	Dithizone	Dithizone (field kit)
Sample 1 (0 µg/l)	0.28	0.50	0.10	1.00	12.60
Sample 2 (4 µg/l)	3.90	4.60	4.00	1.40	9.60
Sample 3 (6 µg/l)	5.40	7.50	5.80	5.00	9.00
Sensitivity	0.1	0.3	0.1	0.5	-

It is apparent from the above brief discussion that the needed data on mercury sorption to be employed in mathematical models must be collected using the mercury analyzer.

E. Hazards of Active Carbon and Coal as Sorbents for Mercury Removal

It is interesting to note that a school of thought (Pendygraft, Schlegel and Huston, 1979) is against the wide-scale use of active carbon and charcoal as sorbents, even for organics removal for which these are so effective. They quoted Joshua Lederberg, a Noble Laureate, warning the U.S. National Drinking Water Advisory Council in 1976, "I have to tell you, you could make a horror story of the chemistry of what is in charcoal. If you were to take charcoal and disaggregate it and hydrogenate it, it would end up with a lot of horror substances that we would really seriously like to avoid. I am not aware of any studies that are specifically

directed to the particular concern and I would most urgently
and most seriously advocate them before we promulgate the
use of charcoal adsorption on a large scale for our public
water supplies." In an experiment, twentyfour metals were
leached from the Virgin granular active carbon, including lead,
mercury, cadmium and arsenic (Pendygraft, Schlegel and Huston,
1979). This leads to the belief that active carbon or coal
is not without blemish as an adsorbent.

4. WEIGHING MODIFIED APPROACHES WITH AVAILABLE DATA

A review of the available sorption models on the basis of data need and preliminary assessment in terms of their applicability to mercury systems (Chapter 2) coupled with a consideration regarding the special aspects related to mercury sorption led to the inclusion of the following approaches for final consideration. These approaches are based on the sorption models discussed in Chapter 2.

Approach A

Second order kinetics using Thomas solution (Thomas, 1944) and supplemented by Hiester and Vermeulen (1952) employing (i) theoretical determination of the sorption rate constant according to Hiester and Vermeulen (1952) and (ii) graphical determination of the sorption rate constant according to Miyamoto and Tram (1979).

Approach B

A modified approach in line with the lumped parameter method used by Keinath (1975) and coupling the diffusion model of Newman (1931).

Approach A

A notable limitation of the Thomas solution is that the model is valid for Langmuir isotherm only. For Freundlich and other isotherms, the model is not applicable. Miyamoto and Tram (1979) also developed their graphical method of predicting the sorption rate constant for conditions satisfying Langmuir isotherm only. Also,

theoretical determination of the sorption rate constant according to Hiester and Vermeulen (1952) is accomplished using Langmuir isotherm data. The Thomas solution (equation 16) was applied to predict effluent concentration-time profiles in the mercury-coal system of Pandey (1978) and mercury-active carbon system of Humenick and Schnoor (1974). The Langmuir isotherm plots for the two systems under consideration are shown in Fig. 3.

Mercury-Coal System

Equilibrium parameter, r, in equation (13) $= \frac{1}{1 + KC_o}$. The calculated equilibrium parameter, r, is nearly unity for $K = 0.3744$ 1/mg (Fig. 3b) and $C_o = 10$ μg/l (Pandey, 1978)

$$\text{Column capacity parameter, } s = \frac{k \, \rho_b \, KSL}{v_1} \qquad (17)$$

$$\text{For } r = 1, \frac{1}{k} = \frac{1}{k_F \, a_F} + \frac{1}{k_p \, a_p \, D_G} ; \qquad (19a)$$

the parameters were defined in equation (19). The column capacity parameter was calculated from the parameters shown in a tabular form in the following page.

$$\text{Ratio of capacity parameters, } \frac{t}{s} = \frac{V - vf_E}{D_G \, vf_E} \qquad (14)$$

For $r = 1$ and $s = 4.75$, $t/s = 0.25$ (from Fig. 2) for break-through ($C/C_o = 10$ percent). To reach breakthrough, it was calculated from equation (14), the time required would be about 27 months for $D_G = 1707.3 \times 10^3$ and $vf_E = 17.64$ cm^3. The period of 27 months for reaching breakthrough is too long a time to accept eventhough the available data

| Parameter	Source of Evaluation	Value
$k_F a_F$	cf. $k_F A_p$ computed in Approach B	0.032/hr
D_G	$\dfrac{q_\infty \, b}{C_o f_E}$	1707.3×10^3
D_p	Pandey (1978)	0.078 cm
ϵ	Pandey (1978)	0.5
D_1	determined in Approach B	2×10^{-9} cm^2/sec
f_I	assumed	0.5
D_{pore}	equation (21)	0.5×10^{-9} cm^2/sec
$k_p A_p$	equation (20)	0.0109549/hr
k	equation (19a)	0.03225/hr
ℓ_b	Pandey (1978)	0.7 g/cm^3
L	Pandey (1978)	45 cm
v_1	Pandey (1978)	8.15 $ml/min/cm^2$
K	Fig. 3	0.3744 1/mg
S	Fig. 3	12.195 mg/g
s	equation (17)	4.75
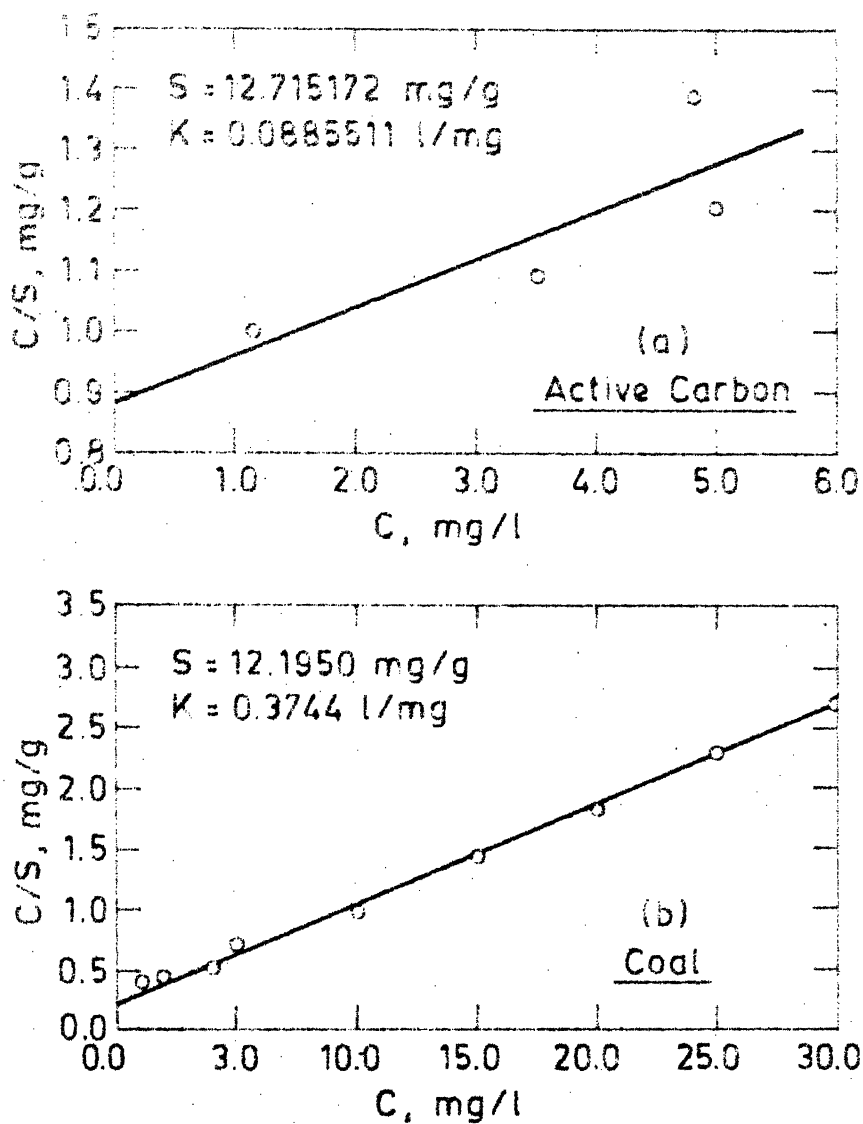
FIG. 3 LANGMUIR ISOTHERM PLOTS FOR MERCURY.

(Pandey, 1978) shows that there was no sign of breakthrough upto run time of 8 days.

Following the graphical approach of Miyamoto and Tram (1979), the value of the rate constant was determined from Fig. 4(b) to be 0.068/hr. The calculated column capacity parameter, s, for this rate constant was 10.02. For r = 1 and s = 10.02, t/s = 0.45 (from Fig. 2) for breakthrough (C/C_o = 10 percent). For breakthrough, the required calculated time (from equation 14) was 49 months which is, again, a totally unacceptable prediction.

Mercury-Active Carbon System

The equilibrium parameter, r, the column capacity parameter, s, and the ratio of the capacity parameter, t/s, were similarly calculated for this system also from the following available data (Humenick and Schnoor, 1974): K = 0.08855 l/mg (Fig. 3a), S = 12.715172 mg/g (Fig. 3a), L = 107 cm, k = 0.05/hr (assumed), v_1 = 9.4 ml/min/cm^2, C_o = 3 mg/l, f_E = 0.5, vf_E = 606.7 cm^3. The column capacity parameter, s, was found to be 2.42 and D_G was calculated as 3840, the latter still being apparently very high. The capacity ratio, t/s, was found to be 0.1 for breakthrough (from Fig. 2). For attaining this breakthrough the required time, calculated from equation (14), was 17 days and 6 hr... Comparing with the available data (Humenick and Schnoor, 1974) it was seen that the predicted results were very encouraging as the breakthrough was not achieved in the actual column even after 5 days.
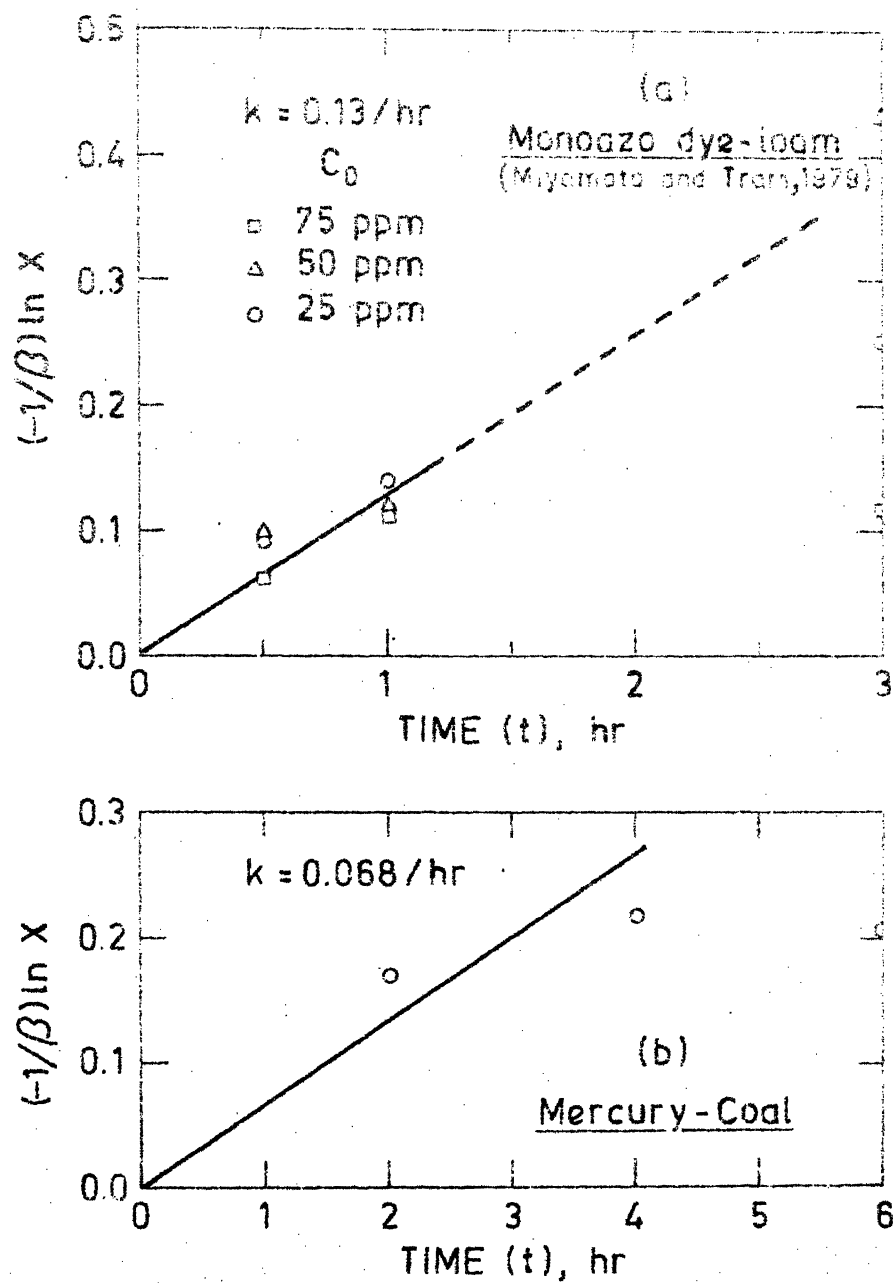
FIG. 4 PLOTS FOR DETERMINING THE RATE CONSTANT.

The fact that the Thomas solution was reasonably applicable to the mercury-active carbon system (C_o = 3 mg/l) and failed miserably in the mercury-coal system (C_o = 10 μ g/l) demonstrates that the influent concentration is a very significant factor and that if it is very low, the approach becomes invalid. From the calculations it is also seen that a very low influent concentration gives an abnormally high value of D_G which ultimately increases the required run time for breakthrough. Eventhough that the breakthrough is not independent of concentration is acceptable, the enormous increase in the theoretical run time required with decreasing concentration only demonstrates that the model is inapplicable in the case of mercury concentrations in the microgram range.

Approach B

A review of the Keinath Model (Keinath, 1975) shows three limitations, viz., (i) the model is not nondimensional, (ii) the CSMP/360 program used for solution is not available with the dec-10 system at I.I.T., Kanpur, and (iii) this model is also limited to Langmuir isotherm conditions only.

The first two limitations were eliminated by proposing a modification of the Keinath model in the nondimensional form and numerically solving the equations by the fourth order Runga-Kutta method. The following lumped parameter model equations developed by Keinath were discussed in Chapter 2.

$$\frac{dC_n}{dt} = (\frac{U}{\varepsilon V}) (C_{n-1} - C_n) - (\frac{\rho}{\varepsilon}) R_A \qquad (11)$$

$$\frac{dq_n}{dt} = R_A \qquad (12)$$

Keinath (1975) discussed in details about the determination of the rate of sorption, R_A, and the rate equations for pore diffusion, pore-surface diffusion and film diffusion were given. Eventhough various theories including the penetration and free surface models have been advanced to describe transient diffusion through an external boundary layer, the straightforward relationship given in the following equation is the only form that is generally applicable to simulation of the dynamics of a columnar adsorber

$$R_A = \frac{dq}{dt} = k_F A_p (C - C^*) \qquad (29)$$

where, k_F = film-diffusion controlled mass transfer coefficient, cm/hr,

A_p = external interfacial transfer area for sorbent, cm^2/g,

C^* = solution-phase concentration of solute considered to be in equilibrium with the outer surface of the sorbent particle, mole/l,

$$= \frac{q}{q_{max}B - q.B} \text{ (for Langmuir isotherm), and} \qquad (30)$$

B = Langmuir energy term, l/hr.

Because of the difficulty in describing the hydrodynamic conditions in the boundary layer, Keinath (1975) determined the mass transfer coefficient, k_F, from a correlation of the mass transfer factor, j_d, with Sherwood number, Reynolds number and Schmidt number as follows

$$j_d = N_{Sh}/N_{Re}(N_{Sc})^{1/3} \tag{31}$$

where, $j_d = (k_F/U)(\mathcal{V}/D_1)^{2/3}$, mass transfer factor,

$N_{Sh} = k_F D_p/D_1$, Sherwood number,

$N_{Sc} = \mathcal{V}/D_1$, Schmidt number,

$N_{Re} = \bar{U}D_p/\mathcal{V}$, Reynolds number,

$\bar{U} = U/A$, velocity of flow, cm/hr, and

$\mathcal{V}$ = kinematic viscosity of solution, cm^2/sec.

The equation used by Keinath (1975) for determining the mass transfer factor, j_d, was

$$j_d = 5.7(N_{Re})^{-0.78} \tag{32}$$

The details of the formulation of the modified non-dimensional approach developed for application in the present study are given below

$$Z_n = \frac{C_n}{C_o} \tag{33}$$

$$Y_n = \frac{q_n}{q_{max}} \tag{34}$$

$$T = \frac{tU}{\varepsilon V} \tag{35}$$

$$E = \frac{1}{C_o B} \tag{36}$$

$$F = \frac{\varepsilon C_o}{\rho\, q_{max}} \tag{37}$$

$$G = \frac{\rho\, v\, k_F}{U} \tag{38}$$

From equations (30) and (34)

$$C^* = \frac{Y}{B(1 - Y)} \tag{39}$$

From equations (33), (36) and (39)

$$Z_n^* = \frac{E\, Y_n}{(1 - Y_n)} \tag{40}$$

Equation (33) through equation (40) were substituted in equations (11) and (12) to obtain

$$\frac{dZ_n}{dT} = (Z_{n-1} - Z_n) - G\left(Z_n - \frac{E\, Y_n}{1 - Y_n}\right) \tag{41}$$

$$\frac{dY_n}{dT} = GF\left(Z_n - \frac{E\, Y_n}{1 - Y_n}\right) \tag{42}$$

The initial conditions: at $T = 0$, $Z = 1$ and $Y = 0$. The details regarding the different parameters used in this model are given in Appendix B.

The fourth order Runga-Kutta method was used for numerical solution of the equations (41) and (42). The program listing for the solution is given in Appendix C.

The coefficient of diffusivity of mercury complexes in solution, D_1, is an important parameter which is difficult to

determine (Section E; Chapter 2). Keinath (1975) did not explain how he calculated D_1 for the present study. D_1 was calculated on the basis of the diffusion model of Newman (1931). From the batch kinetic data of Pandey (1978) and Fig. 1, D_1 was determined as 2×10^{-9} cm^2/sec for the mercury-coal system. The diffusion model-predicted concentrations for a batch sorption system on the basis of this value of the coefficient of diffusivity, D_1, and the experimentally determined concentrations were plotted in Fig. 5. It was interesting to note that although the predicted concentrations were showing an initial higher rate of the decrease in the liquid-phase mercury concentration, after sometime (1-3 hr) the predicted concentrations were higher than the actual concentrations. This showed that when the concentration reduces to a certain limiting value, in addition to diffusion there exists one or more controlling phenomenon. It could well be convection as in the case of the Convection Limited Model of Hendricks (1980) (Section K; Chapter 2). It might be diffusion-convection instead of diffusion-only, which causes greater removal of mercury from liquid phase than the predicted values. This itself shows that the coefficient of diffusivity, D_1, is difficult, if not almost impossible, to determine very accurately for the systems under consideration. Nevertheless, the value of D_1 was accepted (or rather assumed) as $1 - 2 \times 10^{-9}$ cm^2/sec for the mercury-coal system. Similarly, 8×10^{-8} cm^2/sec was considered acceptable for the mercury-active carbon system using the data of Humenick and Schnoor (1974).
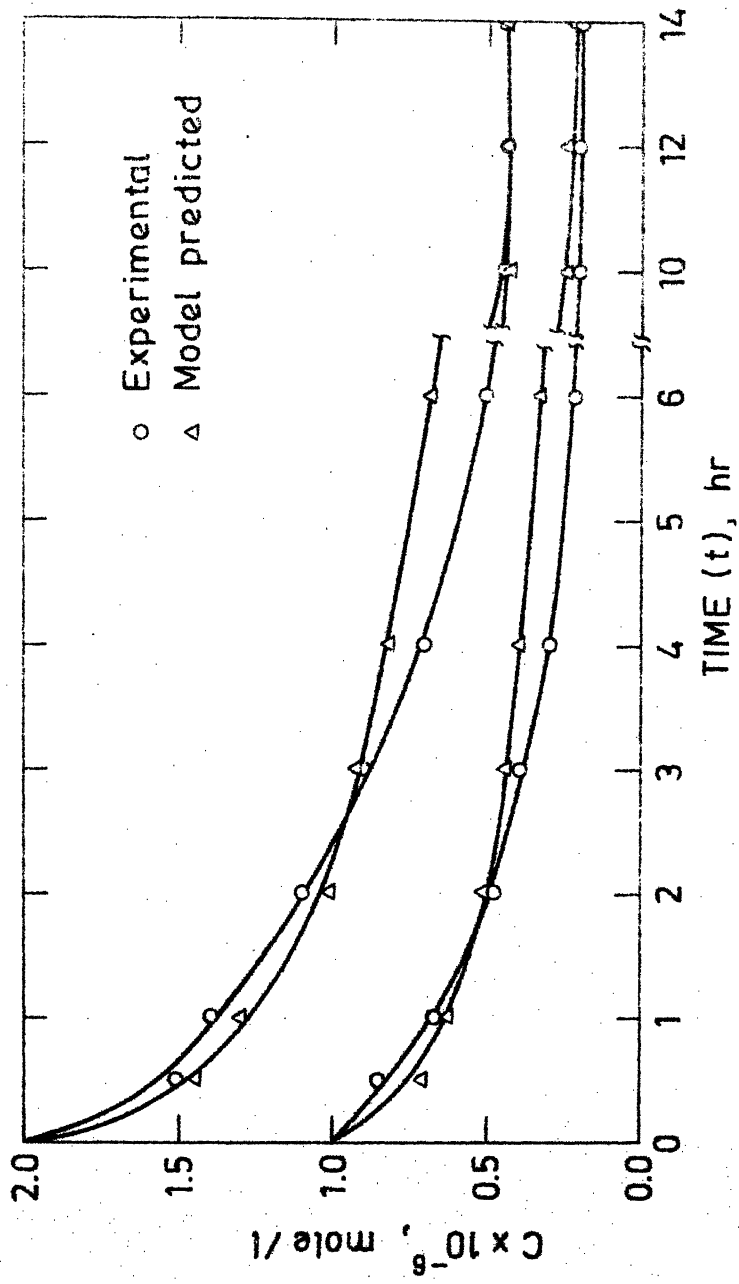
FIG. 5 DIFFUSION MODEL PREDICTED AND EXPERIMENTALLY DETER-
MINED CONCENTRATIONS IN MERCURY-COAL BATCH SORPTION.

On the basis of the different parameters defined in
Appendix B, the numerical solution predicted effluent concen-
tration-time profiles for each of the ten column elements are
shown in Fig. 6. It is seen that for mercury-active carbon
system (Fig. 6a), the predicted breakthrough occurred after
2 days and 7 hr whereas Humenick and Schnoor (1974) in their
experiment could not get the breakthrough even after 5 days.
For mercury-coal system (Fig. 6b), the predicted breakthrough
occurred after 7 days whereas Pandey (1978) could not get the
breakthrough even after 8 days. Unfortunately, data were not
reported for run time beyond 5 and 8 days for the mercury-
active carbon and mercury-coal systems, respectively and hence
the degree of discrepancy could not be ascertained. However,
it could be very well said that the modified lumped parameter
approach predicted an early breakthrough.

The fact that the approach considered included several
significant parameters must be kept in mind while any attempt
is made to criticize its apparent inadequacy per se in terms
of predicting the performance of a real-world system. Para-
meters like the rate coefficient of sorption, diffusivity,
coefficient of mass transfer, etc., are difficult to determine
without reservations. Now, if an approach fails, whether
the blame goes to the conceptual formulation of the approach
or the limitations involved in determination of individual
parameters, is a matter for open discussion. The approach
was based on the lumped parameter method which is widely
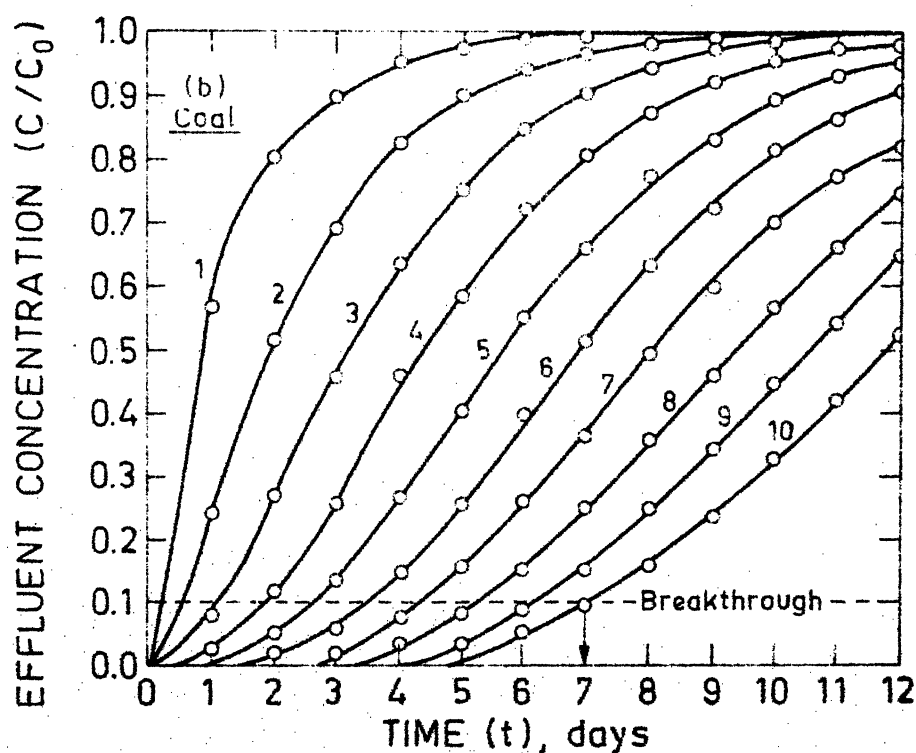used in process dynamics (Friedly, 1972) and has been
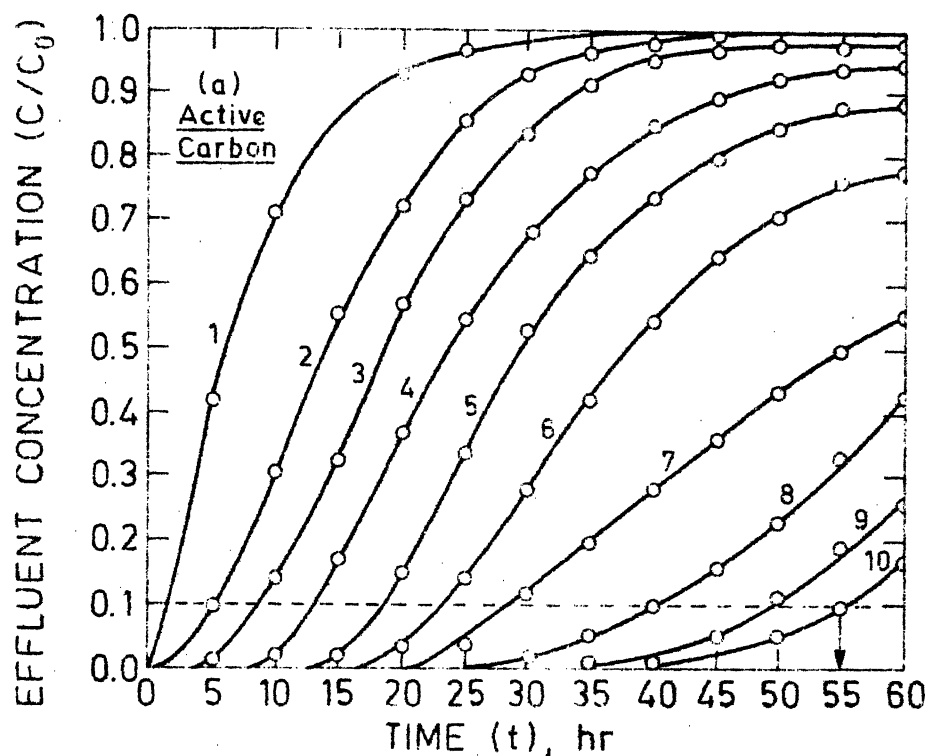
FIG. 6 EFFLUENT CONCENTRATION-TIME PROFILE
FOR MERCURY-ACTIVE CARBON AND
MERCURY-COAL SYSTEMS.

applied by other workers to the sorbent column-system (Wilson and Clarke, 1979). So one has to make sure that the significant parameters are evaluated in a reliable manner before blaming the approach.

Lack of reliability in evaluating the mass transfer coefficient, k_F, and the effective area of transfer, A, prevents precise weighing of the Approach B. One way of making an acid test of the successful applicability of the approach would be as follows: (i) for a particular system like the mercury-coal or mercury-active carbon system, experimental data are to be collected for different sets of influent concentration, velocity of flow, etc.,(ii) for one such set, the value of $k_F A$ may be determined using the model and other known parameters required, (iii) this $k_F A$ may be considered to be constant for the particular system, (iv) with this value of $k_F A$ and other known parameters, the concentration-time profile may be predicted for other sets of influent concentration, velocity of flow, etc., and (v) comparison of this predicted profile with the experimental one would give a good idea about the success of the approach.

Keinath (1975) reported the predicted effluent concentration-time profiles only and did not include a comparison with the experimental profiles. Also, he did not indicate the CPU time required for running the program in the computer. Thus whether Approach B could give better results than the original lumped parameter method of Keinath (1975) solved by CSMP/360, could not be ascertained. Eventhough the

concept of the lumped parameter model as such might be without blemish, the fact that the model contains so many parameters is its main drawback.

It is important to recognize that the set of differential equations (Equations (41) and (42)) are extremely stiff, i.e., the time constant for the liquid-phase equation is small in contrast to the time constant for the solid-phase equation. Numerical solution by the Runga-Kutta method required specification of an integration interval that provided for the stable and accurate integration of the liquid-phase mass balance equation which responded most rapidly. As during the computation it was seen that the increase of the integration interval beyond 0.10 and 0.004 for mercury-coal and mercury-active carbon, respectively, gave rise to instability, the computations were done with these intervals which ultimately required pretty high CPU times.

In spite of all these minus points, it should be recognized that the Keinath model is very useful as a starting point for any modified approach. Keinath (1975) himself hoped that the model would provide for the development of a generalized descriptive model which can be employed as a tool for understanding the complicated phenomenon of sorption.

5. SUMMARY AND CONCLUSIONS

A good number of sorption models are available in the literature, most of them being related to organics sorption. None of these models were proposed for or applied to heavy metal sorption. To facilitate easy predictions of the removal of mercury by active carbon or coal in a column system, investigations were made to find a reliable and handy choice from the listing of the available models. The available information on mercury species distribution in solution was studied and the importance of electrokinetic interaction, that had so far been neglected, was recognized. It was thought that the sizes of different mercury complexes should also be investigated into for predicting to what extent these would enter the micropores of the sorbent. The preliminary screening, based mainly on the availability of suitable data, eliminated all but only a couple of the available models, viz., the Thomas solution and the Keinath model. The latter was modified to the nondimensional form and as the library-program originally used was not available, the equations were solved by the fourth order Runga-Kutta method. Also, an approach based on the second order kinetics using Thomas solution and employing a theoretical as well as a graphical determination of the sorption rate constant was included. These constituted the major portion of the investigation. It was recognized that the crux of the problem, which did not permit satisfactory testing of the approaches considered,

was inability to reliably evaluate the significant parameters involved.

Considering the fact that the present study is a step forward in the area of modeling heavy metal sorption, it is not possible to totally accept any available model or propose a new model. It may be concluded without hesitation, however, that none of the available organics sorption models is acceptable for predicting mercury removal by active carbon or coal without major modifications.

6. SUGGESTIONS FOR FURTHER WORK

1. The important parameters like electrokinetic interaction as well as species distribution and the size effects of the different probable mercury complexes in solution should be incorporated into any model for better simulation of mercury removal, in spite of the computational complicacy that would be brought in by such incorporation.

2. Any available model limited to Langmuir isotherm conditions only should be modified for application to other common isotherm conditions like Freundlich, BET, etc.

3. Appreciating that the sorption rate constant for Thomas solution of the second-order kinetics is of utmost importance, efforts should be made to evaluate the rate constant on the basis of more reliable experimental data.

4. The liquid-film mass transfer coefficient may be calculated by the application of the modified Keinath model (Approach B) with the available sorption data on the basis of trial and error by tuning the computer. Once the transfer coefficient is found for a particular system, it may be used to predict effluent concentration-time profiles for the same system.

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APPENDIX A

LIST OF MATHEMATICAL SYMBOLS

The following symbols were used

A_p = external interfacial transfer area for sorbent, cm^2/g,

a = original amount of sorbate, mg/l,

a_F = effective area for mass transfer for case of fluid-phase transfer controlling, cm^2,

a_p = effective area for mass transfer for case of transfer inside solid particles, cm^2,

B = Langmuir energy term, l/hr,

C_o = influent concentration of solution-phase in a column system or initial concentration of solution-phase in a batch system, mole/l or mg/l,

$\bar{C}, C$ = solution-phase concentration of solute, mg/l,

C_∞ = solution-phase concentration of solute at equilibrium, mg/l,

D = molecular diffusivity, cm^2/sec,

D_G = limiting distribution coefficient,

D_l = diffusivity of solute in solvent, cm^2/sec,

D_p = sorbent particle diameter, cm,

D_{pore} = pore diffusivity, cm^2/sec,

f_E = external porosity,

f_I = internal porosity,

$H(z)$ = error function,

I_o = modified Bessel function of the first kind,

j_d = mass transfer factor,

k = sorption rate constant, hr^{-1},

k_F = mass transfer coefficient for case of fluid-phase transfer controlling, cm/hr,

k_p = mass transfer coefficient for case of transfer inside solid particles, cm/hr,

K = Langmuir isotherm constant, l/mg,

K' = sorption rate constant, hr^{-1},

L = length of column, cm,

N = sorption capacity coefficient,

N_{Re} = Reynolds number,

N_{Sc} = Schmidt number,

N_{Sh} = Sherwood number,

n = an integer,

n = number of elements in the lumped parameter model,

Q = ultimate sorbent capacity, mg/g,

q = solid-phase concentration of solute, mg/g,

q_∞ = solid-phase concentration of solute at equilibrium, mg/g,

r = sorbent particle radius, cm,

r = equilibrium parameter in Thomas solution,

R = volumetric flow rate of fluid through fixed sorbent, ml/min,

R_A = rate of sorption, mole/g-hr,

S = ultimate capacity of dry sorbent, mg/g,

s = amount of sorbate sorbed per unit weight of sorbent at saturation, mg/g,

s = column-capacity parameter in Thomas solution,

t = time, hr,

t = solution capacity parameter in Thomas solution,

U = solution volumetric flow rate, l/hr,

$\bar{U}$ = velocity of flow, cm/hr,

V = total volume of feed in column in Thomas solution, ml,

V = volume of each element in lumped parameter model, l,

V = batch volume of liquid in Famularo model, l,

v = approach velocity, l/hr,

v = bulk volume of column under consideration, ml,

v_1 = macroscopic water flow velocity, $ml/cm^2/hr$,

x, x_t = amount of sorbate sorbed per unit weight of sorbent, mg/g,

x_d = bed depth in Logistic curve model, cm,

x_∞, x_{eqm} = amount of sorbate sorbed per unit weight of sorbent at saturation, mg/g,

x_1, x_2 = amount of sorbate sorbed per unit weight of sorbent at time t_1 and t_2 respectively, mg/g,

z = axial distance, cm,

b = density of dry sorbent in column, g/cm^3,

ε = solid-solution ratio, mg/l, and

η = kinematic viscosity of solution, cm^2/sec.

APPENDIX B

PARAMETER INPUTS: MODIFIED KEINATH MODEL

		Coal (Pandey, 1978)	Active Carbon (Humenick and Schnoor, 1974)
CARBON =	mass of carbon/coal in bed, g	24.74	550.0
A =	external transfer area for carbon/coal, cm^2/g.	35.00	150.0
DP =	diameter of carbon/coal particles, cm	0.078	0.118
RHO =	packed bed density, g/l	700.0	453.23
EPSI =	packed bed porosity	0.50	0.45
QMAX =	Langmuir ultimate uptake capacity, moles/g	6.098×10^{-5}	6.357×10^{-5}
B =	Langmuir energy term, l/mole	0.749×10^{5}	0.177×10^{5}
CO =	solution-phase concentration of solute, mole/l	0.5×10^{-7}	1.5×10^{-5}
DL =	diffusivity of solute, cm^2/sec,	1.22×10^{-9}	8.0×10^{-8}
AREA =	cross-sectional area of column, cm^2	0.785	11.341
U =	solution volumetric flow rate, l/hr	0.384	6.396
E =	nondimensional parameter	267.094	3.764
F =	nondimensional parameter	0.586×10^{-6}	0.234×10^{-3}
G =	nondimensional parameter	8.422	631.285

APPENDIX C

COMPUTER PROGRAM

```
C          -------------------MODIFIED KEINATH MODEL-----------------------

C                          Mercury-Coal System
           REAL KO,K1,K2,K3
           DIMENSION X(20),X1(20),X2(20),X3(20),FX(20),
           1KO(20),K1(20),K2(20),K3(20)
           COMMON E,F,G
           OPEN(UNIT=1,FILE='MPP2.RES')
           DATA E/.2670940E+03/,F/.5857157E-06/,G/.84216937E+01/
           DELT=0.10
           KKF=8000
C          ===============================================================
C          INITIALIZATION:-
C          ----------------
           T=0.0
           DO 8 I=1,20
8          X(I)=0.0
           KK=0
C          ---------------------------------------------------------------
           TYPE 1
           WRITE(1,1)
1          FORMAT(49X,'KEINATH MODEL MERCURY-COAL SYSTEM'//42X,
           1'CONCENTRATION PROFILES IN SIMPLE PACKED BED COLUMN'/
           242X,50('='))
           TYPE 2,E,F,G,KKF,DELT
           WRITE(1,2),E,F,G,KKF,DELT
2          FORMAT (//1X,'E=',E14.7,2X,'F=',E14.7,2X,'G=',E14.7,2X,
           1'KKF=',I6,2X,'DELT=',F5.3)
C          ---------------------------------------------------------------
100        CALL DERIV(X,FX)
           DO 10 I=1,20
           KO(I)=FX(I)*DELT
10         X1(I)=X(I)+0.5*KO(I)

           CALL DERIV(X1,FX)
           DO 11 I=1,20
           K1(I)=FX(I)*DELT
11         X2(I)=X(I)+0.5*K1(I)

           CALL DERIV(X2,FX)
           DO 12 I=1,20
           K2(I)=FX(I)*DELT
12         X3(I)=X(I)+K2(I)
```

```
        CALL DERIV(X3,FX)
        DO 19 I=1,20
19      K3(I)=FX(I)*DELT

        DO 25 I=1,20
25      X(I)=X(I)+(K0(I)+2.*K1(I)+2.*K2(I)+K3(I))/6.0
        T=T+DELT
        KK=KK+1
        SUMQ=0.0
        DO 60 I=11,20
        SUMQ=SUMQ+X(I)
60      CONTINUE
        IF(KK.NE.KKF) GO TO 100
        TYPE 5,T,SUMQ,(X(I),I=1,20)
        WRITE(1,5),T,SUMQ,(X(I),I=1,20)
5       FORMAT(/1X,'T=',F11.3,2X,'SUM Y(N)=',E15.7/1X,'Z',10E13.7/
        11X,'Y',10E13.7)
        KK=0
        PAUSE
        GO TO 100
        STOP
        END
C--------------------------------------------------------------
        SUBROUTINE DERIV(U,DU)
        DIMENSION U(20),DU(20),P(10)
        COMMON E,F,G
        DO 10 I=1,10
10      P(I)=G*(U(I)-(E*U(I+10)/(1.0-U(I+10))))
        DU(1)=(1.0-U(1))-P(1)
        DU(11)=F*P(1)
        DO 20 I=2,10
        DU(I)=(U(I-1)-U(I))-P(I)
        DU(I+10)=F*P(I)
20      CONTINUE
        RETURN
        END
C--------------------------------------------------------------
```